



(11) Publication number: **0 545 081 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **92118701.9**

(51) Int. Cl.⁵: **G03F 7/035**

(22) Date of filing: **01.11.92**

(30) Priority: **01.11.91 US 786564**

(43) Date of publication of application:
09.06.93 Bulletin 93/23

(84) Designated Contracting States:
BE DE FR GB IT

(71) Applicant: **HERCULES INCORPORATED**
1313 N. Market Street Hercules Plaza
Wilmington Delaware 19804 (US)

(72) Inventor: **Mayes, Richard Thomas**
262 South Dillwyn Road
Newark, DE 19711 (US)

(74) Representative: **Lederer, Franz, Dr. et al**
Lederer, Keller & Riederer, Patentanwälte,
Lucie-Grahn-Strasse 22
W-8000 München 80 (DE)

(54) **Carboxyl-containing plasticizers in dry-film photopolymerizable compositions.**

(57) **An aqueous-developable dry-film photopolymerizable composition is disclosed wherein the photopolymerizable composition contains a carboxyl-containing polyurethane having at least one ethylenically unsaturated end group as a plasticizer.**

EP 0 545 081 A1

The present invention relates to aqueous-developable dry-film photopolymerizable compositions useful as photoresists.

Aqueous-developable dry-film photopolymerizable compositions can be used in the manufacture of printed circuits boards. Such photopolymerizable compositions are generally made by applying the solvated resist material to a carrier, such as a transparent polyester film, and then evaporating the solvent to produce the dry film. For example, US-A-4,886,171 and US-A-4,725,524 disclose aqueous developable photopolymerizable compositions in the form of dry films. In typical use as a photoresist, a dry-film photopolymerizable composition is applied to a copper-clad substrate along with the carrier, exposed in certain areas through the carrier to actinic radiation that will cure the film, and then washed with an alkaline aqueous solution to remove the unexposed film from the copper. The exposed copper surface can then be removed in etching solutions leaving the protected area under the cured photopolymerizable composition to form the electrical circuit. US-A-3,469,982 US-A-4,283,635, and US-A-4,268,810 disclose examples of the photoimaging techniques and equipment, including radiation sources, exposure intensity and duration, developing and stripping solutions and techniques, and laminated board compositions.

Photopolymerizable compositions intended as photoresists are preferably designed to keep exposure time and development time to a minimum as well as to ensure that the photopolymerizable composition is preferentially adhesive to the carrier material as opposed to the cover material. It is also important to maintain flexibility in the material after curing so the cured material does not crack or break during processing.

However, a delicate balance of ingredients must be maintained in photopolymerizable composition formulations. Materials that advantageously affect flexibility of the resist, even when used in small amounts, might easily adversely affect exposure time or development time or might adversely affect the preferentially adhesive character of the composition. Plasticizers such as N-ethyl-toluene sulfonamide have been incorporated into photopolymerizable composition formulations in order to increase flexibility. However, such plasticizers can leach out of the composition, which limits their effectiveness.

According to the present invention there is provided in an aqueous-developable dry-film photopolymerizable composition, the improvement wherein the photopolymerizable composition further comprises a carboxyl-containing polyurethane having at least one ethylenically unsaturated end group as a plasticizer. Ethylenic unsaturation in the polymer allows it to react with other materials in the photopolymerizable composition during photopolymerization, thereby becoming part of the cured matrix. Flexibility of the cured material is thereby improved since the plasticizer, as part of the cured matrix, will not leach out of the material. Carboxyl groups increase the polymer's solubility, which facilitates removal of the polymer from uncured areas during washing. The present invention also provides an article comprising the dry-film photopolymerizable composition disposed on a carrier. The present invention further provides in a method of using an aqueous-developable dry-film photopolymerizable composition comprising the steps of applying to a substrate the photopolymerizable composition disposed on a carrier, imagewise exposing (that is, exposing through a negative) the photopolymerizable composition through the carrier to actinic radiation sufficient to cure the photopolymerizable composition in exposed areas, removing the carrier from the photopolymerizable composition, and washing the photopolymerizable composition with an alkaline aqueous solution to remove uncured photopolymerizable composition from the substrate, the improvement wherein the photopolymerizable composition further comprises the carboxyl-containing polyurethane having at least one ethylenically unsaturated end group.

Aqueous-developable dry-film photopolymerizable compositions are well known in the art, and specific components thereof and their relative amounts in addition to the polyurethane plasticizer that are useful in accordance with the present invention will be readily apparent to the skilled artisan. "Dry" films are those in which solvent has been evaporated. In an embodiment of the present invention, the photopolymerizable composition includes a carboxyl group-containing, film-forming polymeric binder, a free-radical photoinitiator, a polyfunctional addition-polymerizable monomer, and a thermal polymerization inhibitor in addition to the polyurethane plasticizer. Other optional additives are also useful, such as adhesive promoting agents. Based on the total weight of the dry-film photopolymerizable composition: the amount of polymeric binder varies from 30-75%, more preferably from 45-60%; the amount of photoinitiator varies from 2-10%, more preferably from 3-7%; the amount of addition-polymerizable monomer varies from 5-40%, more preferably 15-25%; the amount of polyurethane plasticizer varies from 0.5-30%, more preferably from 2-30%, and most preferably from 9-15%; and the amount of thermal polymerization inhibitor varies from 0.003%-0.04%, more preferably from 0.01%-0.02%.

The polyurethane useful as plasticizer in accordance with the present invention has a preferable acid number (that is, the number of milligrams of KOH need to neutralize one gram of the polymer) of 1-150, more preferably 2-140, most preferably about 10, and a preferable molecular weight of 5,000-50,000, more preferably 15,000-25,000. The polyurethane is preferably made by (1) reacting a mixture of at least two aliphatic diols and an aliphatic dihydroxy mono- or dicarboxylic acid with an excess of an aliphatic, cyclo-aliphatic or aromatic

diisocyanate in the presence of a catalyst to produce an isocyanate-terminated urethane polymer having free carboxyl groups on the polymer backbone, and (2) reacting the terminal isocyanate groups of the product of step (1) with an aliphatic monohydroxy methacrylate.

The mixture of diols used in step (1) of the preferred process includes at least two aliphatic diols, preferably those having a weight average molecular weight of 1000 to 4000. Suitable aliphatic diols include polyethylene glycol; polypropylene glycol; a block copolymer made by reacting a propylene oxide polymer with ethylene oxide; polytetrahydrofuran diol; polypropylene adipate diol; neopentyl glycol adipate diol; 1,4-butanediol ethylene glycol adipate diol; 1,6-hexanediol phthalate adipate neopentyl glycol phthalate adipate diol and ethylene glycol adipate diol. The mixture of diols also includes an aliphatic dihydroxy mono- or dicarboxylic acid. Suitable dihydroxy carboxylic acids include bis-hydroxymethylpropionic acid, 2,3-dihydroxybutanoic acid; 2,4-dihydroxy-3, 3-dimethylbutanoic acid; 2,3-dihydroxyhexadecanoic acid; dihydroxy-butanoic acid, tartaric acid and 2,3-dihydroxy-2-methyl-propionic acid. The concentration of hydroxy-functional carboxylic acid can be varied from 0.2% to 30%, preferably from 2% to 5%, based on the total weight of the components used to prepare the urethane polymer.

The mixture of diols is reacted with an excess of an aliphatic, cycloaliphatic or aromatic diisocyanate. Suitable diisocyanates include, for example, 2,4- or 2,6-toluene diisocyanate; isophorone diisocyanate; 1,6-hexamethylene diisocyanate; 2,2,4-trimethylhexamethylene-1,6-diisocyanate; p,p'-methylene-bis-phenylisocyanate or mixtures thereof.

The equivalent hydroxyl to isocyanate ratio for the reaction can vary from 1.1 to 2.0. The reaction temperature is preferably from 40°C to 90°C, most preferably from 70°C to 80°C. The reaction is preferably carried out in the presence of 50 to 300 ppm of an organic tin compound or from 0.1 to 3% of an aliphatic amine compound as a catalyst. Suitable catalysts include, for example, dioctyltin bis(isooctylmercaptoacetate), dibutyltin dilaurate, dibutyltin diisooctylmaleate, triethylenediamine, triethanolamine and triethylamine.

The urethane polymer that is formed is characterized by the presence of free carboxylic acid groups on the backbone of the polymer and isocyanate groups at the ends of the polymer chain.

In the second step of the reaction, the product from step (1) is reacted with an aliphatic monohydroxy acrylate or methacrylate in an amount sufficient to react with the isocyanate groups at the ends of the polymer chain. From 0.2 to 10 equivalents of excess hydroxy-functional methacrylate are preferred. Suitable acrylates and methacrylates include, for example, 2-hydroxypropyl acrylate and methacrylate, butanediol monoacrylate and monomethacrylate, polyethylene glycol (10-20 moles ethylene oxide) monoacrylate and monomethacrylate and polypropylene glycol (5-20 moles propylene oxide) acrylate and methacrylate. An organic tin compound or an aliphatic amine compound of the types and amounts specified above can be used as a catalyst for this reaction if desired. The resulting urethane polymer is a liquid, has acrylate or methacrylate groups on the ends of the polymer chain, free carboxyl groups on the polymer backbone, and an acid number of 1 to 150.

The free-radical photoinitiator useful in accordance with this invention is a conventional photoinitiator activatable by actinic radiation that is thermally inactive below about 185°C. Exemplary photoinitiators are aromatic ketones, such as benzophenone and dimethoxyphenyl acetophenone. Other useful photoinitiators will be apparent to those skilled in the art.

The polyfunctional addition-polymerizable monomer that finds application in the subject invention is non-gaseous, contains at least 2, preferably 2 to 4, more preferably 2 to 3 ethylenic double bonds. Having at least 2 ethylenic double bonds makes the monomer polyfunctional, i.e., capable of cross-linked polymerization. Suitable monomers include alkylene or polyalkylene glycol diacrylates. Monomers containing vinylidene groups conjugated with ester linkages are particularly suitable. Illustrative examples include but are not limited to ethylene diacrylate; diethylene glycol diacrylate; glycerol diacrylate; glycerol triacrylate; 1,3-propanediol dimethacrylate; 1,2,4-butanetriol trimethacrylate; 1,4-benzenediol dimethacrylate; 1,4-cyclohexanediol diacrylate; pentaerythritol tri- and tetramethacrylate; pentaerythritol tri- and tetraacrylate; tetraethylene glycol dimethacrylate; trimethylolpropane trimethacrylate; triethylene glycol diacrylate; tetraethylene glycol diacrylate; pentaerythritol triacrylate; trimethylolpropane triacrylate; pentaerythritol tetraacrylate; 1,3-propanediol diacrylate; 1,5-pentanediol dimethacrylate; and the bis-acrylates and bis-methacrylates of polyethylene glycols, polypropylene glycols, and copolymers thereof of molecular weight from about 100 to about 500 (number average). Other useful polymerizable monomers will be apparent to those skilled in the art.

The thermal polymerization inhibitor useful in accordance with the instant invention prevents thermal polymerization during drying and storage. Examples of useful thermal polymerization inhibitors are p-methoxyphenol, hydroquinone, alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, β-naphthol, 2,6-di-tert-butyl-p-cresol, 2,2'-methylene-bis(4-ethyl-6-tert-butylphenol), p-tolylquinone, chloranil, aryl phosphites, and aryl alkyl phosphites. Other useful thermal polymerization inhibitors will be apparent to those skilled in the art.

The carboxyl group containing film-forming polymeric binder useful in accordance with this invention is prepared from one or more film-forming, vinyl type monomers and one or more alpha, beta ethylenically unsaturated carboxyl group containing monomers having 3-15 carbon atoms, which makes the binder soluble in aqueous media. Examples of useful vinyl type monomers are alkyl and hydroxyalkyl acrylates and methacrylates having 3-15 carbon atoms, styrene, and alkyl substituted styrenes. Examples of useful carboxyl group-containing monomers are cinnamic acid, crotonic acid, sorbic acid, acrylic acid, methacrylic acid, itaconic acid, propionic acid, maleic acid, fumaric acid, and half esters and anhydrides of these acids. Other useful binders will be apparent to those skilled in the art.

In one embodiment, a monofunctional carboxyl group-containing addition polymerizable monomer is added to the photopolymerizable composition of the instant invention. The monofunctional (i.e., containing one ethylenic double bond) carboxyl group containing monomer is used because the photopolymerized material made from the photopolymerizable composition is then strippable from a substrate in small pieces. Without this monomer, the photopolymerized material strips well, but in large sheets. Stripping in small pieces is preferred since the photopolymerized material between fine lines is more easily removed. Also, some stripping apparatuses have filtration systems that could have clogging problems if stripping occurs in large sheets. Based on the weight of the photopolymerizable composition of the instant invention, the amount of the monofunctional carboxyl group-containing addition-polymerizable monomer used is preferably from about 1% to about 10%, more preferably from about 1.5% to about 6%. Useful monofunctional carboxyl group-containing addition-polymerizable monomers are, for example, itaconic acid, beta-carboxyethylacrylate, citraconic acid, crotonic acid, monomethacryloyloxyethyl phthalate, monoacryloyloxyethyl phthalate, and fumaric acid. Other useful monomers will be apparent to those skilled in the art.

The photopolymerizable composition of this invention optionally includes additives well known in the art of photopolymerizable compositions, such as leuco (i.e., printout) dyes, background dyes, adhesion promoters, and antioxidants. Other optional additives will be apparent to those skilled in the art. While desirable, the optical additives are not essential to the instant invention.

The photopolymerizable composition of this invention is prepared by mixing the various components in a solvent. Suitable solvents are alcohols, ketones, halogenated hydrocarbons, and ethers. Other solvents will be apparent to those skilled in the art. After mixing, the composition is then coated onto a support or carrier, and the solvent is evaporated. The photopolymerizable composition has a preferable thickness of 25.4 to 50.8 μm . Carriers are preferably about 0.0254-0.0508 mm thick. The photopolymerizable composition of this invention, i.e., as rolls of dry film sandwiched between a flexible support member and a flexible cover member. It will be apparent to those skilled in the art that dry films of the instant invention can be made on inflexible supports as well as flexible supports and may be supplied as stacks of laminated sheets.

The photopolymerizable composition of this invention is used as a photopolymerizable composition in the manufacture of printed circuit boards. Generally, the composition is applied onto the copper surface of a copper clad substrate, exposed to actinic radiation through a negative to create a latent image of photopolymerized material, and developed in a known aqueous developing solution to remove the unpolymersed composition from the copper surface. The portions of the surface not covered by the photopolymerized material are then modifiable by known processes, e.g., by plating or etching procedures, while the photopolymerizable composition protects the covered surface. The photopolymerized material can be ultimately removed from the substrate by washing with known stripping solutions.

The photopolymerizable composition of the instant invention is applied to the copper clad substrate by known procedures, such as hot shoe or hot roll lamination of the dry film attached to a transparent, peelable support, which support is removed after polymerization. Generally, the amount of actinic radiation used to polymerize the composition varies from about 35 to about 150 mJ/cm², with precise amounts determinable by those skilled in the art based on the specific composition used.

The copper clad substrate is any known copper/dielectric laminate used in circuit board manufacture, such as a copper clad board of fiberglass reinforced epoxy resin. Other useful dielectrics will be apparent to those skilled in the art.

The aqueous developing solutions used in accordance with this invention have, by weight, about 0.5-10% alkaline agents, preferably about 0.5-1%, and the latent imaged board is washed in the solution for a time sufficient to remove the unpolymersed composition. Useful alkaline agents are alkali metal hydroxides, e.g., lithium, sodium and potassium hydroxide, the base reacting alkali metal salts of weak acids, e.g., sodium carbonate and bicarbonate, and alkali metal phosphates and pyrophosphates. The circuit board can be submerged in the developing solution or, preferably, the solution is high pressure sprayed on the board.

In general, the stripping solutions useful in removing the photopolymerized material in accordance with the instant invention are heated aqueous alkaline solutions, using the same alkaline agents as the developing solutions, but having a higher alkaline concentration, i.e., generally, by weight, from about 1%-10%, preferably

from about 1%-3%. Generally, the stripping solution is heated to a temperature of about 45°C-65°C, preferably about 50°C-55°C. Washing the substrate to remove the photopolymerized material is by methods well known to those skilled in the art, such as spraying the substrate with the heated stripping solution or, preferably, agitating the substrate in a heated bath of the stripping solution.

In order to more clearly describe the present invention, the following non-limiting examples are provided. All parts and percentages in the examples are by weight unless indicated otherwise.

EXAMPLE 1

A polyurethane useful in accordance with the present invention was made according to the following formulation.

Table 1

	<u>Equiv.</u>	<u>wt.</u>	<u>Equiv.</u>
	<u>wt.</u>	<u>%</u>	
polypropylene glycol ¹	995	29.28	0.0294
block copolymer ²	996	42.63	0.0428
bis-hydroxymethyl- propionic acid	67	2.37	0.0353
toluene diisocyanate	87.1	14.07	0.1619
2-hydroxypropyl methacrylate	144	3.88	0.0269

¹weight average molecular weight 2,000, available from Olin Chemical Co. under the name Poly G 55-53.

²weight average molecular weight 2,000, made by reacting ethylene oxide with a propylene oxide polymer and available from Olin Chemical Co. under the name Poly G 20-56.

The polypropylene glycol, block copolymer and bis-hydroxymethyl-propionic acid were dried under a nitrogen purge for 12 hours at approximately 60°C. Dioctyltin bis(isooctylmercaptoacetate) catalyst (0.015%) was added, followed by the toluene diisocyanate. The reaction mixture, still under nitrogen, was heated to 75° to 80°C. Samples were taken for isocyanate analysis. At 1.8% isocyanate, the 2-hydroxypropyl methacrylate containing 0.10% butylated hydroxytoluene as a stabilizer and 0.015% of the same tin catalyst were added under an air atmosphere. The final product had an acid number of 10.2.

EXAMPLE 2

This example demonstrates a dry film photopolymerizable composition made in accordance with the present invention that is provided as a roll of material in which the resist is sandwiched between a polyester carrier film and a polyethylene cover film.

A photopolymerizable composition was prepared using the following ingredients: 77 parts acrylate polymer (31% solids) 13% ethyl acrylate, 65% methyl methacrylate, 22% methacrylic acid, made as in Synthesis Example of U.S. Pat. No. 4,985,343, except that methyl ethyl ketone (MEK) was used instead of isopropyl alcohol, and the final material was adjusted to 31% solids; 0.23 parts adhesion agent (molecular weight 22,000, partially hydrolyzed hydroxyl-modified vinyl chloride/vinyl acetate copolymer, about 90% vinyl chloride, 4% vinyl acetate, 2.3% hydroxyl content, available under the name UCAR VAGD from Union Carbide.); 3% methoxylated Bisphenol A dimethacrylate (available under the name BPE 500 from skin-Nakamura Chemical Co. Ltd.); 2.9 parts urethane polymer from Example 1; 7 parts trimethylolpropane triacrylate (Sartomer Chemical Co.) 1.5 parts dimethoxyphenyl acetophenone (Ciba-Geigy); 0.3 parts isopropyl thioxanthone (Aceto Chemical Co.); 1.5 parts ethyl dimethylaminobenzoate (Aceto Chemical Co.); 0.6 parts pentabromomono-chlorocyclohexane (PCBH, available from Nissei Chemical Company, Japan); 0.6 parts ethoxylated ethylene diamine (available under the name QUADROL from BASF Corporation, Chemical Division, Parsippany, NJ); 0.02 parts butylated hydroxytoluene; 0.4 parts itaconic acid; 0.08 parts diethanolamine-modified tolyl triazole (available

under the name REOMET 42 from Ciba-Geigy Corporation, Hawthorne, NY); 0.05 parts first dye solution (2.44% Brilliant Green, 6.27% Victoria Blue, and 91.29% methanol); 0.4 parts second dye solution (5% Brilliant Green and 95% methanol); and 0.2 parts Leuco Crystal Violet. The composition was mixed thoroughly, and coated on a 92 gauge transparent polyester film to thickness of about 38.1 μm . The material was then dried in an oven to remove the solvent. The dried photopolymerizable composition was then laminated with a 25.4 μm thick polyethylene film and rolled into a roll around a cylindrical core.

EXAMPLE 3

This example demonstrates a further embodiment in accordance with the present invention in which a dry film photopolymerizable composition is provided as a roll of material in which the resist is sandwiched between a polyester carrier film and a polyethylene cover film.

A photopolymerizable composition was prepared using the following ingredients: 78 parts acrylate polymer (31% solids) as in Example 2; 0.23 parts adhesion agent (molecular weight 27,000, partially hydrolyzed hydroxyl-modified vinyl chloride/vinyl acetate copolymer, about 90% vinyl chloride, 4% vinyl acetate, 2.3% hydroxyl content, available under the name UCAR VAGD from Union Carbide.); 3% glycerol propoxy triacrylate; 2.9 parts urethane polymer from Example 1; 7 parts trimethylolpropane triacrylate; 2.5 parts benzophenone; 0.13 parts Michler's ketone; 1.5 parts ethyl dimethylaminobenzoate; 0.6 parts pentabromomonochlorocyclohexane; 0.6 parts ethoxylated ethylene diamine; 0.02 parts butylated hydroxytoluene; 0.08 parts diethanolamine-modified tolyl triazole; 0.05 parts first dye solution (2.44% Brilliant Green, 6.27% Victoria Blue, and 91.29% methanol); 0.4 parts second dye solution (5% Brilliant Green and 95% methanol); and 0.2 parts Leuco Crystal Violet. The composition was mixed thoroughly and rolls of dry film were made as in Example 2.

EXAMPLE 4

A urethane polymer was prepared. Under nitrogen at 60°C, a mixture of 37.01 parts polypropylene glycol (as in Example 1), 53.88 parts block copolymer (as in Example 1), and 2 parts tartaric acid were dried overnight. The mixture was then cooled to about 45-55°C, and 0.015 weight% dioctyltin bis(isooctylmercaptoacetate) catalyst was added followed by 13.36 parts toluene diisocyanate in three equal increments. After 30 minutes the reaction mixture was heated to 70°C while still under nitrogen. The OH/NCO equivalent ratio was 1:1.3. Samples were taken for isocyanate analysis. At 1.5-2.0% isocyanate, 7.65 parts 2-hydroxypropyl methacrylate and 0.015 weight% of the tin catalyst along with 0.10 weight% butylated hydroxytoluene as a stabilizer were added under an air atmosphere. The temperature was then raised to approximately 75°C until NCO content is less than about 0.1-0.3%. The final product had an acid number of 18.

EXAMPLE 5

This example demonstrates an embodiment in accordance with the present invention using the urethane polymer from Example 4 as a plasticizer.

A photopolymerizable composition was prepared using the following ingredients: 78 parts acrylate polymer (31% solids) as in Example 2; 0.23 parts adhesion agent (molecular weight 27,000, partially hydrolyzed hydroxyl-modified vinyl chloride/vinyl acetate copolymer, about 90% vinyl chloride, 4% vinyl acetate, 2.3% hydroxyl content, available under the name UCAR VAGD from Union Carbide.); 3% glycerol propoxy triacrylate; 2.9 parts urethane polymer from Example 4; 7 parts trimethylolpropane triacrylate; 2.5 parts benzophenone; 0.13 parts Michler's ketone; 1.5 parts ethyl dimethylamino-benzoate; 0.6 parts pentabromomonochlorocyclohexane; 0.6 parts ethoxylated ethylene diamine; 0.02 parts butylated hydroxytoluene; 0.08 parts diethanolamine-modified tolyl triazole; 0.05 parts first dye solution (2.44% Brilliant Green, 6.27% Victoria Blue, and 91.29% methanol); 0.4 parts second dye solution (5% Brilliant Green and 95% methanol); and 0.2 parts Leuco Crystal Violet. The composition was mixed thoroughly and rolls of dry film were made as in Example 2.

Claims

1. In an aqueous-developable dry-film photopolymerizable composition, the improvement wherein the photopolymerizable composition further comprises a carboxyl-containing polyurethane having at least one ethylenically unsaturated end group, and is present in an amount of 0.5-30% based on the weight of the dry film photopolymerizable composition.

2. The photopolymerizable composition of claim 1 wherein the polyurethane has an acid number of 2-140.
3. The photopolymerizable composition of any of the preceding claims comprising the polyurethane, a carboxyl group-containing, film-forming polymeric binder, a free-radical photoinitiator, a polyfunctional addition-polymerizable monomer, and a thermal polymerization inhibitor.
4. The photopolymerizable composition of any of the preceding claims wherein the polyurethane has a methacrylate or acrylate end group at each end of the polymer chain.
5. An article comprising the dry-film photopolymerizable composition of any of the preceding claims disposed on a carrier.
6. The article of claim 5 wherein the article comprises the photopolymerizable composition sandwiched between a flexible carrier film and a flexible cover film.
7. The article of claims 5 or 6 wherein the polyurethane is present in an amount of 2-30%, based on the weight of the dry-film photopolymerizable composition.
8. The article of claims 5, 6 or 7 wherein the photopolymerizable composition comprises the hydroxyl-modified vinyl chloride/vinyl acetate polymer, a carboxyl group-containing, film-forming polymeric binder, a free-radical photoinitiator, a polyfunctional addition-polymerizable monomer, and a thermal polymerization inhibitor.
9. The article of claims 5, 6, 7 or 8 wherein the polyurethane has a methacrylate end group at each end of the polymer chain.
10. In a method of using a dry-film photopolymerizable composition comprising the steps of applying to a substrate an aqueous-developable dry-film photopolymerizable composition disposed on a carrier, exposing the photopolymerizable composition imagewise through the carrier to actinic radiation sufficient to cure the photopolymerizable composition in exposed areas, removing the carrier from the photopolymerizable composition, and washing the photopolymerizable composition with an alkaline aqueous solution to remove uncured photopolymerizable composition from the substrate, the improvement wherein the photopolymerizable composition further comprises a carboxyl-containing polyurethane having at least one ethylenically unsaturated end group, and is present in an amount of 0.5-30% based on the weight of the dry-film photopolymerizable composition.
11. The method of claim 10 wherein the polyurethane has an acid number of 2-140.
12. The method of claims 10 and 11 wherein the photopolymerizable composition comprises the polyurethane, a carboxyl group-containing, film-forming polymeric binder, a free-radical photoinitiator, a polyfunctional addition-polymerizable monomer, and a thermal polymerization inhibitor.
13. The method of claims 10, 11 or 12 wherein the polyurethane has a methacrylate or acrylate end group at each end of the polymer chain.
14. In a composition comprising a carboxyl group-containing, film-forming polymeric binder, a free-radical photoinitiator, polyfunctional addition-polymerizable monomer, a thermal polymerization inhibitor, and a solvent, the improvement wherein the composition further comprises a carboxyl-containing polyurethane having at least one ethylenically unsaturated end group, and is present in an amount of 0.5-30% based on the weight of the composition without the solvent.
15. The composition of claim 14 wherein the polyurethane has an acid number of 2-140.
16. The composition of claims 14 or 15 wherein the polyurethane has a methacrylate or acrylate end group at each end of the polymer chain.

EP 0 545 081 A1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8701

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 452 139 (HERCULES INCORPORATED) * page 2, line 48 - line 56 *	1-16	G03F7/035
Y,D	EP-A-0 233 623 (HERCULES INCORPORATED) * page 2, line 2 - line 6 * * page 3, line 6 - line 7; claims *	1-9, 14-16	
Y	EP-A-0 125 862 (ASAHI KASEI KOGYO KABUSHIKI KAISHA) * claims 8-15 *	10-13	
<p style="text-align: center;">-----</p>			<p>TECHNICAL FIELDS SEARCHED (Int. Cl.5)</p> <p>G03F</p>
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01 FEBRUARY 1993	Examiner DUPART J-M.B.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

EPO FORM 501 (01/92)